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(54) **Detergent tablets**

(57) A detergent tablet is disclosed which comprises at least 50 wt% of a non-phosphate builder and from 0 to 20 wt% of a phosphate builder, and has incorporated therein as binder from 0.3 to 5 wt% of a neutralised polymer of hydrophilic or hydrophobic monomers which have a glass transition temperature (T<sub>g</sub>) of from 40 to

120°C, which monomers comprise(meth)acrylic acid, maleic anhydride, hydroxyalkyl(meth)acrylic acids, alkyl(meth)acrylates, alkylhydroxy(meth)acrylates, alkyl(meth)acrylic acids or styrene, the polymer having a weight average molecular weight of from 10,000 to 120,000. The tablet has improved physical properties compared with those of the prior art.

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## Description

The present invention relates to detergent tablets and bars, and more specifically to tablets and bars of detergents which contain high levels of non-phosphate ingredients.

In the past, phosphates have been used in detergents generally to avoid calcium salt precipitation. Detergents containing phosphates could be made with the same formulation in both powder and tablet form, because phosphates impart good tabletising properties. However nowadays phosphates are generally used in detergents either at very low levels or not at all, and instead other builders such as zeolite, citrates, silicates, layered silicates, disilicates etc are employed. These builders are generally available in powder or granular form, and can easily be dry mixed or granulated in powdered detergent formulations. However their granulometry and other physical properties are such that tabletising the powder formulation is very difficult. Hence in order to tabletise such formulations, it has generally been necessary to reformulate the detergent, or to add binding agents to the powder before tabletising.

Examples of such binding agents include fatty alcohols or fatty acids such as lauryl alcohol or stearic acid. For example GB 989683A discloses coating a detergent tablet with a water-soluble film-forming polymer such as polyvinyl alcohol. However they are generally difficult to use because they are solids at room temperature, and also reduce the dissolution rate of the tablet, which is undesirable in a detergent.

Other binders used include sodium salts of homo- or copolymeric (meth)acrylic acid, as disclosed in EP 579659A, which are agglomerated with the other components of the detergent, the agglomerate then being dried and tableted. Tablets produced with such binders have improved physical and solubilization properties; however these properties are still capable of improvement to be comparable with those of tablets which do contain phosphate builders for example.

To manufacture bar or tablet detergents extrusion is often used, and manufacturers frequently experience difficulties in maintaining satisfactory mechanical resistance in the bars, which often break during production, handling or storage.

An alternative to incorporating binders within a formulation to be tableted is to tablet the formulation and then coat the tablet with a compound which will improve its resistance to breakage and rapid dissolution. However tablets which have only an external coating of such a material tend to dissolve too rapidly once the outer coating has been removed during the wash, which results in inferior washing results. Furthermore, coating a preformed tablet is of course an extra step in the manufacturing process, which is not preferred. GB 2040980 discloses coating a detergent tablet with polyoxyalkylene nonionic surfactants, although in this case the coating is present for its surfactant properties.

Thus there is a need for a detergent tablet containing high levels of non-phosphate builder which has suitably robust physical properties, particularly which is non crumbling and non dusting, which can be manufactured economically, and which provides detergency results as good as or better than existing tablets. We have discovered that such a tablet can be achieved by tableting a particulate detergent formulation which has been pre-mixed with a particular range of polymeric binders, such that the binder material is incorporated throughout the tablet, rather than only on the surface.

Accordingly in one aspect the present invention provides a detergent tablet which comprises at least 50 wt% of a non-phosphate builder and from 0 to 20 wt% of a phosphate builder, having incorporated therein as binder from 0.3 to 5 wt% of a neutralised polymer of hydrophilic or hydrophobic monomers which have a glass transition temperature (T<sub>g</sub>) of from 40 to 120°C, which monomers comprise(meth)acrylic acid, maleic anhydride, hydroxyalkyl(meth)acrylic acids, alkyl (meth)acrylates, alkylhydroxy (meth)acrylates, alkyl (meth)acrylic acids, or styrene, the polymer having a molecular weight of from 10,000 to 120,000. By "incorporated therein" we mean that the binder is distributed throughout the body of the tablet, and is not just a coating on the surface.

The inorganic builder preferably comprises citrates, silicates, disilicates, zeolite, carbonates, bicarbonates. Other organic chelants may also be employed.

A further aspect of the invention provides a process for producing a detergent tablet which comprises the steps of a) agglomerating a composition comprising at least 50 wt% of a non-phosphate builder and from 0 to 20 wt% of a phosphate builder, and from 0.3 to 5 wt% of a neutralised polymer of hydrophilic or hydrophobic monomers which have a glass transition temperature (T<sub>g</sub>) of from 40 to 120°C, which monomers comprise(meth)acrylic acid, maleic anhydride, hydroxyalkyl(meth)acrylic acids, alkyl (meth)acrylates, alkylhydroxy (meth)acrylates, alkyl (meth)acrylic acids, or styrene, the polymer having a molecular weight of from 10,000 to 120,000, and then b) tableting the resulting agglomerate.

The amount of phosphate builder if present may be 5 wt% or less; preferably it is from 0 to 1 wt%, and more preferably from 0 to 0.1 wt%.

It is necessary for the polymer to be neutralised in order for it to be soluble. The molecular weight of the polymer is preferably from 25,000 to 95,000, most preferably from 40000 to 50000, and its T<sub>g</sub> preferably between 40 and 100°C. Preferred levels in the tablet are from 0.5 to 2 wt%.

Detergent tablets made according to the invention are found to have excellent physical properties compared with known tablets having high levels of non-phosphate builders.

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### EXAMPLES

Dishwashing tablet formulation A	
(all amounts are percentages by weight)	
Sodium citrate dihydrate	35
Carbonate	8
Perborate	10
Tetraacetylenediamine (TAED)	3
Na salt of polyacrylic acid (MW 4500)	4.5
Nonionic surfactant (Plurafac LF 403)	1
Bicarbonate	38-38.5
Tableting aid	0-0.5

Dishwashing tablets were formulated according to the above formulation, each containing a different tableting aid, as listed in Table I below. The tablets were then evaluated visually and also for hardness using a Schleuninger tablet tester 60. The results are given below. Hardness was evaluated after one hour's ageing, and is measured in kPa. MMA = methyl methacrylate, MAA = methacrylic acid, BA = butyl acrylate, HEMA = hydroxyethylmethacrylate, EHA = 2-hydroxyethylacrylate

TABLE I

Tableting aid	Mw	Hardness	Tg	Visual appearance
None		0		Impossible to tabletise
0.5% water		3.5		Wet and crumbling
47MMA/25BA/18MAA/10HEMA	45000	20.5	95°C	Excellent
47MMA/25BA/18MAA/10HEMA	88000	13.0	98°C	Acceptable
47MMA/25BA/18MAA/10HEMA	116000	5.0	100°C	Wet and crumbling
47MMA/25BA/18MAA/10HEMA	148000	5.0	99°C	Very crumbling
52.5MMA/29.5BA/18MAA	20000	17.0	80°C	Good
40 Styrene/30EHA/25AN/5MAA	55800	12.5	51°C	Acceptable
80EHA/20AA	15000	11.0		Acceptable
62BMA/38AA	10000	4.5		Wet and crumbling
Polyurethane		2.5		Wet and crumbling

"Acceptable", "Good" and "Excellent" refer to the tablet's hardness and resistance to crumbling and also to the visual impression. "Acceptable" for instance means that although a proper tablet is formed, the edges of the tablet are not very sharp and the surface is somewhat uneven.

### II - DISHWASHING TABLETS FORMULATED ACCORDING TO EP 579659A

Formulation B was prepared according to the teaching of EP 579659A, and then evaluated for its physical properties with added tableting aid. The tableting aid employed had the formulation 47MMA/25BA/18MAA/10HEMA, Mw 45000, Tg about 98°C.

FORMULATION B:	
Sodium carbonate	46.7%
Sodium sulphate	1%
Copolymer dry*	10.2%
Sodium citrate	10.3%
Sodium disilicate	20.5%
Sodium perborate monohydrate	7.1%
TAED	2.1%

\*sodium salt of a copolymer of acrylic and maleic acid

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FORMULATION B:	
Nonionic surfactant	2.1%

	HARDNESS	Comments	Visual aspect
FORMULATION A + 0.5% water	tablet broken	capping	medium
FORMULATION B + 0.5% tableting aid	15.0	no capping	good

By "capping" is meant that after pressing the top and bottom surfaces of the tablet are compressed by the pressing machine to such an extent that they detach from the body of the tablet as laminar portions, the main body of the tablet being of a less solid consistency.

### III - WASHING TESTS

The above mentioned formulations were tested for performance in comparison with commercially available tablets.

Commercial tablet 1 contains:

<5% nonionic surfactant  
5-15% oxygenated bleach  
>30% phosphate  
enzymes

Commercial tablet 2 contains:

<5% nonionic surfactant  
5-15% oxygenated bleach, polycarboxylate  
enzymes, carbonate, citrate, activator, perfume

Conditions : 1 tablet/wash

Soil : milk + margarine

Water : 600 ppm hardness as  $\text{CaCO}_3$

Scale: 0 = perfect

4 = heavy filming on glasses

DETERGENT	Commercial tablet 1	A - no tableting aid	A + 0.5% tableting aid
QUANTITIES	25.5 g	23.8 g (as powder)	23 g
Filming/spotting 4 cycles	0/1	1/1	0/0
Filming/spotting 8 cycles	0.5/1	1.5/1.5	1/0

Note: Formulation A does not contain enzymes which would improve performance.

### IV - DETERGENCY

Evaluations were made of wood patches impregnated with tea. Thin strips of wood, laminated on one side with plastic, were impregnated on the other side with tea, and the whiteness of the patch evaluated before and after washing.

	Commercial 1	Formulation A	Formulation A + 0.5% tab aid
Whiteness before washing	77.38	75.56	76.12
Whiteness after washing (higher the better)	80.34	82.86	82.60
Yellow scale before wash	2.85	3.85	3.18

(continued)

	Commercial 1	Formulation A	Formulation A + 0.5% tab aid
Yellow scale after wash (lower the better)	1.67	0.37	0.31

The above results demonstrate that the presence in the formulation of tableting aid does not have a detrimental effect on either detergency performance or bleach stability.

#### V - VARIATION ON FORMULATIONS

A further detergent formulation was prepared with the composition given below, and tablets formulated with 0.5% of the tableting aid were evaluated for hardness.

	C
Citrate	20%
Carbonate	8%
Perborate	10%
TAED	3%
Homopolymer	4.5%
Nonionic surfactant	1%
Bicarbonate	53.5%
Disilicate	0

Results : tablets' hardness after ageing for 1 hour

Formulation	Hardness (kPa)
A + 0.25% Tableting Aid	12
A + 0.5% Tableting Aid	19
B + 0.5% Tableting Aid	20
C + 0.5% Tableting Aid	18

#### VI - DISSOLUTION RATES

Tablets were placed in a wire basket in a typical glass fronted dishwasher, and the time to dissolve completely during a typical washing cycle observed visually.

Commercial 1	22 minutes
Commercial 2	33 minutes
Formulation B	27 minutes
Formulation A + T.Aid	24 minutes
Formulation B + T.Aid	21 minutes

Commercial tablets 1 and 2 start dissolving a little later and then fall apart suddenly when wet. Formulations A + Tableting Aid and B + Tableting Aid dissolve more regularly from the early beginning to the end of wash cycles.

#### Claims

1. Detergent tablet which comprises at least 50 wt% of a non-phosphate builder and from 0 to 20 wt% of a phosphate builder, having incorporated therein as binder from 0.3 to 5 wt% of a neutralised polymer of hydrophilic or hydrophobic monomers which have a glass transition temperature (T<sub>g</sub>) of from 40 to 120°C, which monomers comprise (meth)acrylic acid, maleic anhydride, hydroxyalkyl(meth)acrylic acids, alkyl (meth)acrylates, alkylhydroxy (meth)acrylates, alkyl (meth)acrylic acids or styrene, the polymer having a weight average molecular weight of from 10,000 to 120,000.

2. Process for producing a detergent tablet which comprises the steps of a) agglomerating a composition comprising at least 50 wt% of a non-phosphate builder, optionally up to 20 wt% of a phosphate builder, and from 0.3 to 5 wt% of a neutralised polymer of hydrophilic or hydrophobic monomers which have a glass transition temperature (T<sub>g</sub>) of from 40 to 120°C, which monomers comprise (meth)acrylic acid, maleic anhydride, hydroxyalkyl(meth)acrylic acids, alkyl (meth)acrylates, alkylhydroxy (meth)acrylates, alkyl (meth)acrylic acids or styrene, the polymer having a molecular weight of from 10,000 to 120,000; and then b) tableting the resulting agglomerate.
3. Process or tablet according to claim 1 or 2, wherein the polymer has a molecular weight of from 25,000 to 95,000.
4. Process or tablet according to any preceding claim, wherein the polymer has a molecular weight of from 40,000 to 50,000.
5. Process or tablet according to any preceding claim wherein the amount of phosphate builder is from 0 to 5 wt%.
6. Process or tablet according to claim 5 wherein the amount of phosphate builder is from 0 to 1 wt%, preferably from 0 to 0.1 wt%.
7. Process or tablet according to any preceding claim, wherein the polymer has a T<sub>g</sub> of between 40 and 100°C.
8. Process or tablet according to any preceding claim, wherein the polymer comprises units of methyl methacrylate, butyl acrylate, methacrylic acid, hydroxyethylmethacrylate or 2-hydroxyethylacrylate.
9. Process or tablet according to any preceding claim, wherein the polymer comprises 47 wt% methyl methacrylate, 25 wt% butyl acrylate, 18 wt% methacrylic acid, and 10 wt% hydroxyethylmethacrylate.
10. Process or tablet according to any preceding claim, wherein the inorganic builder comprises citrate, silicate, disilicate, zeolite, carbonate or bicarbonate.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 97 30 4019

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
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Place of search THE HAGUE		Date of completion of the search 13 July 1999	Examiner Loiselet-Talsne, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons &amp; : member of the same patent family, corresponding document</p>			

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**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on  
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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82